

# ZnIr<sub>2</sub>O<sub>4</sub>, a *p*-type transparent oxide semiconductor in the class of spinel zinc-*d*<sup>6</sup>-transition metal oxide

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The authors report on the growth of spinel ZnM(*d*<sup>6</sup>)<sub>2</sub>O<sub>4</sub> (*M*=Co, Rh, and Ir), a *p*-type wide band gap semiconductor by pulsed laser deposition. The band gap of these compounds is determined by the ligand field splitting in the subbands of the metallic *d*<sup>6</sup> cation. Photoemission spectroscopy revealed that the valence band maximum is composed of occupied *t*<sub>2g</sub><sup>6</sup> states. The observed band gap is increasing for higher quantum numbers, being as large as ~3 eV for ZnIr<sub>2</sub>O<sub>4</sub>, which is expected from theoretical predictions. Grown in polycrystalline phase, films of these materials display high conductivity, well above 2 S cm<sup>-1</sup>. © 2007 American Institute of Physics.

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Developments in *p*-type transparent oxide semiconductors (TOSs) are of great importance for new applications as blue or ultraviolet light emitting diodes (LEDs) and transparent electronics.<sup>1,2</sup> Recently, LEDs based on *p*-ZnO are demonstrated by several authors.<sup>3,4</sup> However, *p* doping of ZnO is difficult, requiring delicate film growth techniques at high deposition temperature. Moreover, the moderate carrier densities (order of 10<sup>17</sup>) are still inferior to *n*-type TOSs. Mizoguchi *et al.*<sup>5</sup> reported on spinel ZnRh<sub>2</sub>O<sub>4</sub> as a new class of *p*-type TOSs. In contrast to *p*-ZnO and cuprates as CuAlO<sub>2</sub> (Ref. 6) and SrCu<sub>2</sub>O<sub>2</sub>,<sup>7</sup> high carrier densities can be obtained and no long range order is required for hole conductivity in this material.<sup>8–10</sup>

Transparency of this material is determined by the ligand field splitting of the Rh<sup>3+</sup> 4*d* orbitals due to the octahedral surrounding of six oxygen anions. These orbitals are split into fully occupied *t*<sub>2g</sub><sup>6</sup> and empty *e*<sub>g</sub><sup>0</sup> levels, forming a low-spin state configuration.<sup>5</sup> The band gap is situated in between these levels, which act as valence and conduction bands, respectively. The same effect is also observed in ZnCo<sub>2</sub>O<sub>4</sub>, although the band gap is too small for optical transparency.<sup>11</sup> Based on these results the same behavior for this spinel compound containing iridium can be expected. Moreover, the splitting between the *t*<sub>2g</sub> and *e*<sub>g</sub> levels is supposed to increase on going from 3*d*<4*d*<5*d* metals, i.e., from cobalt to rhodium to iridium. Jørgensen has proposed an empirical formula which allows to estimate the ligand field splitting; Δ=*f**g*, where *f* is a relative number dependent on the ligand and *g* is a function of the metal expressed in eV.<sup>12</sup> The values for *g* increase from 2.26 to 3.35 to 3.97 eV in the case of Co(III) to Rh(III) to Ir(III), respectively. From an estimation of the position of oxygen within the spectrochemical series, the value of *f* should be around 0.9, but variations up to 0.37 are observed.<sup>13</sup> These values suggest an increase of Δ with 50% and 25% from 3*d*- to 4*d*- to 5*d*-transition metals. In the present study we therefore investigate the properties of ZnM<sub>2</sub>O<sub>4</sub> films as TOSs, where *M*=Co, Rh, and Ir.

Commercially available powders (Alfa Aesar) of CoO, Rh<sub>2</sub>O<sub>3</sub>, IrO<sub>2</sub>, and ZnO are used to produce deposition targets

by solid state synthesis. Thin films are deposited by pulsed laser deposition (PLD) using a KrF excimer laser (Lambda Physik Compex 205) at 10 Hz, producing a fluency of 6 J/cm<sup>2</sup> on the target surface. The oxygen partial pressure and deposition temperature are kept at 0.250 mbar and between 773 and 973 K, respectively. X-ray diffraction (XRD) measurements are performed on a Philips X'Pert diffractometer using Cu Kα radiation. Electrical conductivity of the thin films is measured in a van der Pauw four-point probe setup down to 100 K (Quantum Design 6000, physical property measuring system). Seebeck coefficients are obtained by thermopower measurements with temperature differences up to 15 K above room temperature. Optical data are collected with a Varian Cary 50 UV-Vis spectrophotometer and photoemission spectroscopy (PES) experiments are performed using a PHI Quantera Scanning ESCA microprobe.

The phase of the three deposition targets is checked by XRD [Fig. 1(a)]. All peaks of the cobalt and rhodium containing mixtures can be indexed and are identified as spinel ZnCo<sub>2</sub>O<sub>4</sub> and ZnRh<sub>2</sub>O<sub>4</sub>, respectively.<sup>14,15</sup> However, bulk ZnIr<sub>2</sub>O<sub>4</sub> could not be synthesized by solid-state synthesis. Also the attempts to induce a reaction via chemical complexation routes were unsuccessful. The peaks of both binary indicate a ZnO:(IrO<sub>2</sub>)<sub>2</sub> mixture in this target. Using these three targets, films with typical thickness of 100–300 nm are deposited on Al<sub>2</sub>O<sub>3</sub> (0001) and quartz substrates. The diffraction spectra of ZnM<sub>2</sub>O<sub>4</sub> films on Al<sub>2</sub>O<sub>3</sub> (0001) are shown in Fig. 1(b). The (111), (222), and (333) peaks of the spinel structure are visible for all compounds, indicating coherent growth. Quartz glass was used to grow films without any epitaxial relation to the substrate. Figure 1(c) shows the polycrystalline nature of these ZnM<sub>2</sub>O<sub>4</sub> samples. The obtained lattice parameters for ZnCo<sub>2</sub>O<sub>4</sub> and ZnRh<sub>2</sub>O<sub>4</sub> correspond well (Table I) with the values found in literature.<sup>14,15</sup> The lattice spacing of ZnIr<sub>2</sub>O<sub>4</sub> almost equals that of ZnRh<sub>2</sub>O<sub>4</sub>, but no literature data are present for comparison. However, this value can be expected as the size of the ionic radii of rhodium and iridium trivalent cations in a six-coordinated octahedral environment is approximately the same as well.<sup>16</sup>

PES results in Fig. 2 show the electronic structure of the ZnM<sub>2</sub>O<sub>4</sub> polycrystalline thin films. The spectra of the differ-

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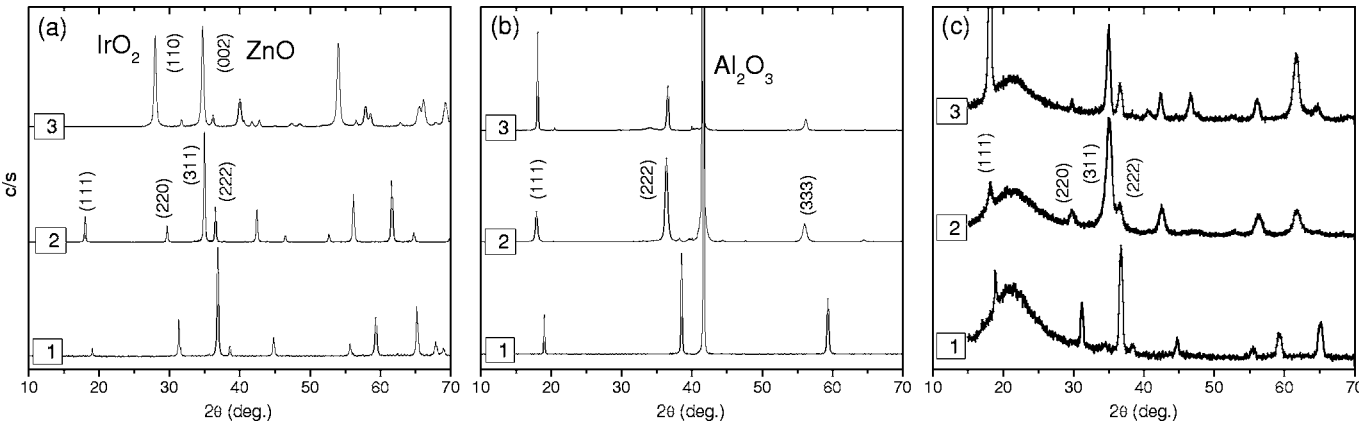


FIG. 1. XRD measurements of cobalt (1), rhodium (2), and iridium containing compounds. Spectra of deposition targets (a), thin films on  $\text{Al}_2\text{O}_3$  (b), and on quartz (c) are shown. Polycrystalline samples on quartz are measured in  $1.5^\circ$  incident angle geometry.

TABLE I. Calculated average lattice parameters of  $\text{ZnM}_2\text{O}_4$  films compared to literature values and ionic radii.

| $\text{ZnM}_2\text{O}_4$  | $\text{Al}_2\text{O}_3$<br>$a$ (Å) | Quartz<br>$a$ (Å) | Literature value<br>$a$ (Å) | Ionic radius<br>(pm) |
|---------------------------|------------------------------------|-------------------|-----------------------------|----------------------|
| $\text{ZnCo}_2\text{O}_4$ | 8.079                              | 8.104             | 8.108                       | 68.5                 |
| $\text{ZnRh}_2\text{O}_4$ | 8.482                              | 8.489             | 8.510                       | 80.5                 |
| $\text{ZnIr}_2\text{O}_4$ | 8.503                              | 8.507             | NA                          | 82.0                 |

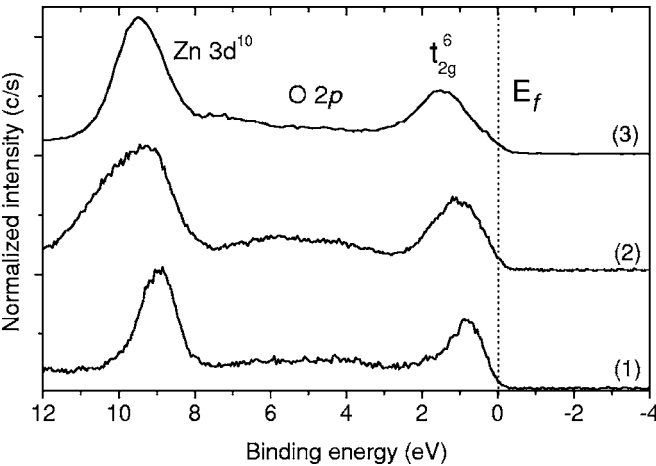


FIG. 2. PES spectra of  $\text{ZnCo}_2\text{O}_4$  (1),  $\text{ZnRh}_2\text{O}_4$  (2), and  $\text{ZnIr}_2\text{O}_4$  (3) films. Data averaged over 5 cycles, resolution of 0.1 eV, and  $\text{Al K}\alpha$  excitation source. Samples are charge neutralized during measurement.

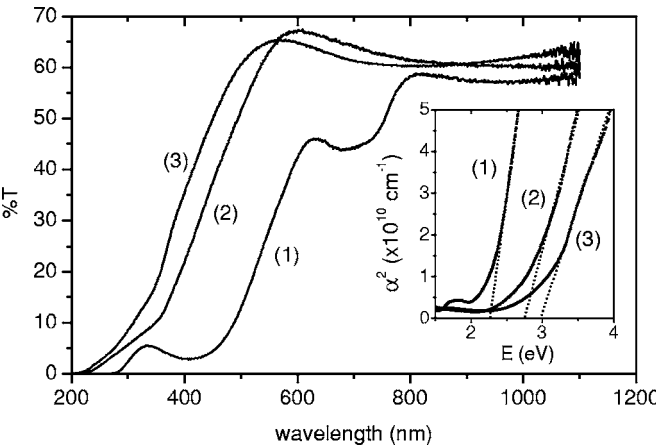


FIG. 3. Optical transmission of  $\text{ZnCo}_2\text{O}_4$  (1),  $\text{ZnRh}_2\text{O}_4$  (2), and  $\text{ZnIr}_2\text{O}_4$  (3) polycrystalline films deposited on quartz. The inset shows the photon energy dependence of  $\alpha^2$  and extrapolation for deducing band gap.

ent compounds look similar and are comparable to reported measurements on  $\text{ZnRh}_2\text{O}_4$ .<sup>5</sup> The band near 10 eV can be identified as  $\text{Zn } 3d^{10}$  and the diffuse region around 5 eV originates from  $\text{O } 2p$  and transition metal band mixing. The high intensity at 1 eV is composed of the  $t_{2g}^6$  states due to the ligand field splitting of  $d^6$  bands of the transition metals. The Fermi level is located at the edge of this valence band maximum indicating  $p$ -type conductivity.

The optical data in Fig. 3 show that the polycrystalline samples containing rhodium and iridium are transparent in the visible region (400–700 nm). The optical gaps obtained from extrapolation of the absorption spectra (inset Fig. 3) are listed in Table II.<sup>17</sup> The primary gap of  $\text{ZnCo}_2\text{O}_4$  is around 2.26 eV, which is somewhat lower than reported by Kim *et al.*<sup>11</sup> However, a similar absorption feature at lower energy ( $\sim 1.5$  eV) is detected. This absorption band is attributed to Co interatomic  $d-d$  transitions associated with a trigonal ligand field splitting.<sup>18</sup> This indicates that a small part of the cobalt ions has interchanged with the tetrahedrally coordinated zinc ions. The cobalt ion can exist in this coordination since the ionic radius is similar to zinc ions.<sup>19</sup> The gap of  $\text{ZnRh}_2\text{O}_4$  of 2.74 eV is larger than earlier observations ( $\sim 2.1$  eV).<sup>5</sup> The smoothness of the absorption spectrum, which is different in our case, can be responsible for this deviation. The obtained optical gap for  $\text{ZnIr}_2\text{O}_4$  is 2.97 eV, making this material most transparent in the visible region. The values scale reasonably with the increase of  $\Delta$  as predicted from the empirical relation mentioned earlier (Table II). The small deviation can be explained by the uncertainty of  $f$  for oxygen ligands. This can be attributed to different bonding lengths due to octahedral distortion.<sup>13</sup> Moreover, somewhat lower measured optical band gap values compared to the predicted electronic gap can be a result of additional states within the band gap.

The electrical properties of the deposited films are listed in Table III. All our samples were found to be highly con-

TABLE II. Optical properties of  $\text{ZnM}_2\text{O}_4$  films. Measured optical gap and predicted electronic gap are both listed.

| $\text{ZnM}_2\text{O}_4$  | $T_{400-700 \text{ nm}}$<br>(%) | $E_{\text{gap}}$<br>(eV) | 0.9g<br>(eV) | Delta gap<br>(%) |
|---------------------------|---------------------------------|--------------------------|--------------|------------------|
| $\text{ZnCo}_2\text{O}_4$ | 26.1                            | 2.26                     | 2.03         | -11              |
| $\text{ZnRh}_2\text{O}_4$ | 54.8                            | 2.74                     | 3.01         | +9               |
| $\text{ZnIr}_2\text{O}_4$ | 60.8                            | 2.97                     | 3.57         | +17              |

TABLE III. Electrical properties of  $\text{ZnM}_2\text{O}_4$  films. Listed values are of polycrystalline films, except for the conductivity referring to polycrystalline as well as epitaxial films.

| $\text{ZnM}_2\text{O}_4$  | $\sigma_{\text{(poly/epi)}}$<br>( $\text{S cm}^{-1}$ ) | Seebeck<br>( $\mu\text{V/K}$ ) | $E_a$<br>(meV) |
|---------------------------|--------------------------------------------------------|--------------------------------|----------------|
| $\text{ZnCo}_2\text{O}_4$ | 0.39/0.61                                              | +131.4                         | 41.7           |
| $\text{ZnRh}_2\text{O}_4$ | 2.75/2.83                                              | +63.4                          | 22.1           |
| $\text{ZnIr}_2\text{O}_4$ | 3.39/2.09                                              | +53.9                          | 46.9           |

ductive (order of  $\sim 1 \text{ S cm}^{-1}$ ). Results of  $\text{ZnCo}_2\text{O}_4$  and  $\text{ZnRh}_2\text{O}_4$  are comparable to the values found by others.<sup>5,11</sup> The conductivity of polycrystalline  $\text{ZnIr}_2\text{O}_4$  is also in this range, which indicates that these three systems are electronically equivalent. In  $\text{ZnCo}_2\text{O}_4$ , a relation between the conduction type ( $p$  or  $n$ ) and the oxygen deposition pressure was shown.<sup>11</sup> Considering the high oxygen deposition pressure we use, doping is introduced by excess oxygen. Additionally, cation vacancies can act as acceptors in the system. The positive Seebeck coefficients confirm the  $p$ -type conduction behavior in all cases [Fig. 4(a) and Table III].

Temperature dependent measurements show an Arrhenius-type behavior [Fig. 4(b)]. The thermal activation energy is estimated from the high temperature region (above 200 K) and is found to be smaller than 50 meV (Table III). So the Fermi level is located close to the valence band in which the dominant carriers (holes) are transported. Although the conductivity at room temperature is rather large, no significant data can be extracted from Hall measurements. Therefore a high carrier concentration combined with low carrier mobility can be expected. This is confirmed by the low values found for the Seebeck coefficient compared to other  $p$ -type oxide semiconductors, induced by higher hole concentrations.<sup>6,7</sup>

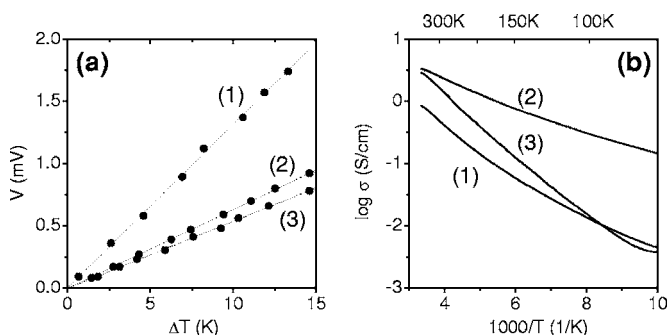


FIG. 4. Thermopower (a) and temperature dependent conductivity measurements (b) of  $\text{ZnCo}_2\text{O}_4$  (1),  $\text{ZnRh}_2\text{O}_4$  (2), and  $\text{ZnIr}_2\text{O}_4$  (3).

In conclusion, we prepared films of spinel  $\text{ZnM}_2\text{O}_4$  ( $M=\text{Co}$ ,  $\text{Rh}$ , and  $\text{Ir}$ ) by PLD. The  $d^6$  bands of these transition metals in octahedral coordination are split due to the field strength of the oxygen ligands. This splitting mainly determines the band gap. An expected increase of this gap for increasing quantum number was confirmed. The observed gap of  $\text{ZnIr}_2\text{O}_4$  is  $\sim 3 \text{ eV}$ . The films containing  $\text{Rh}$  and  $\text{Ir}$  are good candidates for  $p$ -type TOSs. In the case of iridium, the highest transmission has been observed. From PES and Seebeck measurements,  $p$ -type conduction behavior was confirmed for all compounds. The room temperature conductivity of polycrystalline  $\text{ZnIr}_2\text{O}_4$  samples was above  $2 \text{ S cm}^{-1}$ .

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